Determination of the Molecular Orientation of a Phthalocyanine Derivative in a Langmuir–Blodgett Film by Polarized UV–VIS Spectra

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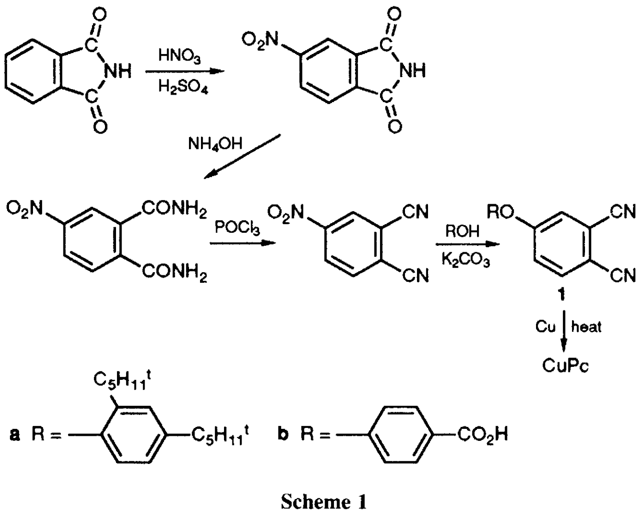
Langmuir–Blodgett (LB) films of (*p*-carboxyphenoxy)-tri(2,4-di-*tert*-pentyl phenoxy)phthalocyanine copper(II) (asyCuPc) are prepared; the associated forms of the compound in chloroform solution and the particular orientation of asyCuPc molecular macrocycles in LB films is determined by polarized UV–VIS.

Phthalocyanines, being thermally and chemically stable, have been widely used as photoconductors, gas-sensors and molecular electronic devices. The preparation of ultrathin and highly ordered Langmuir–Blodgett (LB) films by the LB technique has only recently gained interest. The structure of the LB film must be characterized in order to study the relevant mechanism and to realize its potential application. LB films of our compound have been deposited on a gold-comb electrode by the LB technique in the form of a Z-type semiconductor. The films have been shown to have good sensitivity and selectivity for ammonia vapour. These films, therefore have potential in gas-sensor development.

The copper phthalocyanine (Fig. 1) was synthesized as shown in Scheme 1.

Elemental analysis and spectroscopic data (^{1}H NMR, ESR, IR and electronic) are consistent with the assigned structure. The π–A isotherm of the compound is also shown in Fig. 1. The LB monolayers of asyCuPc were transferred using a Langmuir balance (Model JC-1) (Jilin University of China). The subphase was distilled water with pH *ca.* 5.4. A chloroform solution (2.27×10^{-4} mol dm^{-3}) of asyCuPc was spread onto the water surface. The substrates onto which the LB films were deposited were CaF_2 of 2 mm thickness for UV–VIS measurement, which were cleaned and hydrophobically or hydrophilically (for X-type) treated in the conventional procedure. The monolayer was deposited when the substrate was moving downwards for X type; upwards and downwards for Y type; upwards for Z type. The X, Y, Z types of asyCuPc LB films with 35 layers were deposited at the same pressure of 30 Pa and dipping speed of 8 mm min^{-1}. A UV–VIS spectrum of a solution of the compound in chloroform and polarized spectra of the LB films were observed using a Shimadzu UV-3000 UV–VIS spectrophotometer.

A UV–VIS spectrum of an asyCuPc solution in chloroform is shown in Fig. 2. The characteristic absorption peak



Scheme 1

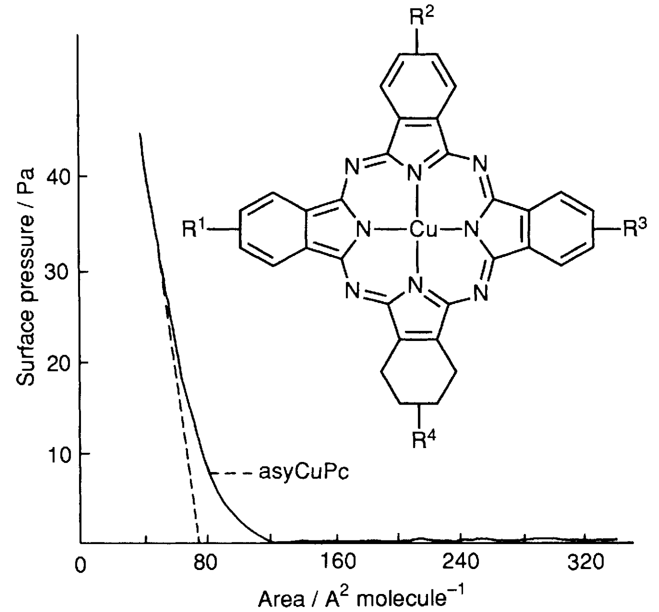
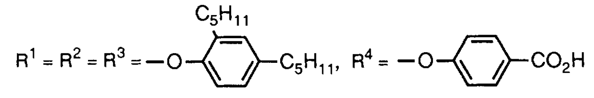


Fig. 1 Structure of the copper phthalocyanine derivative



$R^1 = R^2 = R^3 = -O-C_6H_3(C_5H_{11})-C_5H_{11},\ R^4 = -O-C_6H_4-CO_2H$

and area isotherm of the compound at 20 °C

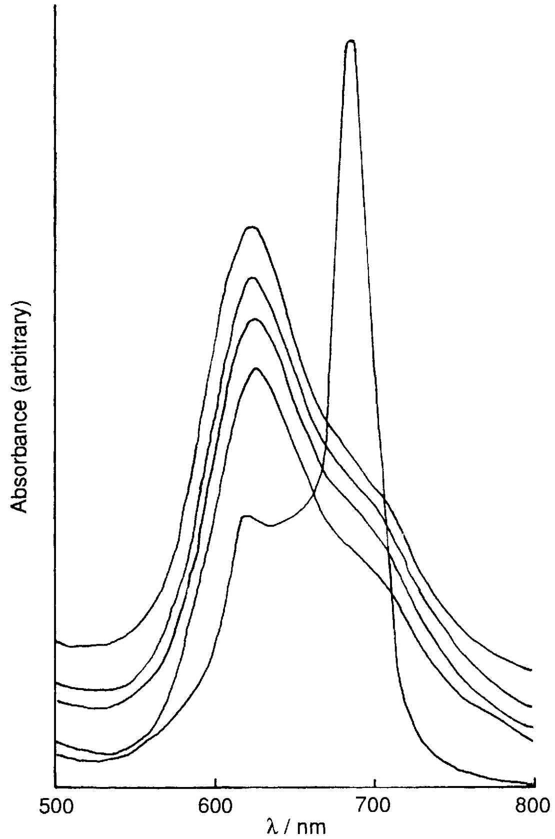


Fig. 2 Typical UV–VIS absorbance of asyCuPc in chloroform solution and polarized absorption spectra of Y-type LB film with electric vectors perpendicular (⊥) and parallel (//) to the dipping direction for 0° and 30° incident angles, respectively

(1) Solution
(2) ⊥ 30°, A = 0.351 at 621 nm
(3) // 30°, A = 0.353 at 621 nm
(4) ⊥ 0°, A = 0.336 at 621 nm
(5) // 0°, A = 0.314 at 621 nm

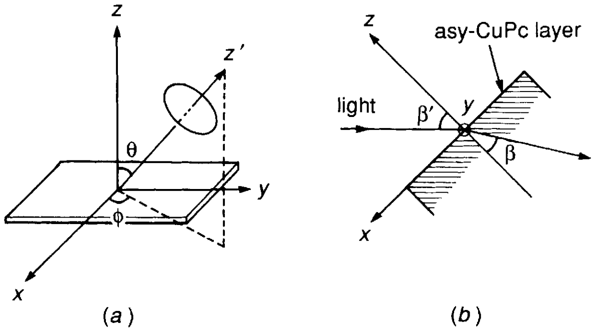


Fig. 3 (*a*) Coordinates (*x*, *y*, *z*) for expressing the CuPc orientation, *y*-axis: dipping direction, *z*-axis: centre axis of CuPc represented by the circular plate. (*b*) Direction of polarized incident light on the substrate.

observed in asyCuPc solution at approximately 680 nm has been assigned to phthalocyanine ligand-centred π–n* transition and shows that monomers dominate in chloroform solution. The weak peak at 621 nm is due to the existence of a small amount of associated species in solution. Fig. 2 also shows polarized spectra of Y-type LB film of asyCuPc and the characteristic band at 621 nm is obviously enhanced and is explained by asyCuPc molecules existing mainly in associated species and the amount of monomers being considerably reduced in the film.

In order to study the orientation of asyCuPc molecular macrocycles in LB film, the phthalocyanine ring is considered as a flat circular plate on which π–π* transition dipole is uniformly distributed according to Yoneyama and Sugi,[1] see eqns. (1), (2) and (3).

$$\langle\cos^2\theta\rangle = \frac{D_0 - (1 + D_0\sin^2\beta)\,D_{30}}{(1\text{–}2\sin^2\beta)\,D_{30} - (1 + D_{30}\sin^2\beta)D_0} \qquad (1)$$

$$\langle\sin^2\theta\cos^2\phi\rangle = \frac{D_0 - \langle\cos^2\theta\rangle}{1 + D_0} \qquad (2)$$

$$D\beta = A_{//}/A_{\perp} \qquad (3)$$

Where $A_{//}$ and $A_{\perp}$ are the absorbance of the film for polarized light with electric vectors both parallel (//) and perpendicular (⊥) to the dipping direction, respectively. The dichroic ratio $D\beta$ can be expressed as eqn. (4).

$$D\beta = [\langle\cos^2\phi\rangle + \langle\cos^2\theta\sin^2\phi\rangle]/[\{\langle\sin^2\phi\rangle + \langle\cos^2\theta\cos^2\phi\rangle\} \times \cos^2\beta + \langle\sin^2\theta\rangle\sin^2\beta] \qquad (4)$$

The coordinates and meanings of the parameters in the equations and also the optical geometry of our experiment are given in Fig. 3 with incidence angles of $\beta' = 0°$ and $\beta' = 30°$.

The refraction angle $\beta = \sin^{-1}(n^{-1}\sin^{-1}\beta')$ and refraction index in the film $n = 1.39$.[2] $A_{//}$ and $A_{\perp}$ can be obtained from polarized UV–VIS spectra. From eqn. (3) the dichroic ratios D_0 and D_{30} can be calculated, and from eqns. (1) and (2) the orientational angles θ and ϕ can be derived. The experimental data and calculation results are listed in Table 1.

The macrocycle plane of asyCuPc molecules is skew to the substrate plane and the molecular orientation of asyCuPc in different types of LB films is almost always the same, this is mainly due to the asymmetric structure of the molecules. *p*-Carboxyphenoxy is a shorter substituent compared with 2,4-di-*tert*-pentyl phenoxy. While asyCuPc molecules are laid on the water surface at zero pressure, asyCuPc molecules prefer to 'lie flat'. Because surface pressure begins to increase at the area of 160 Å^2 in the Fig. 1 and 160 Å^2 is exactly the

Table 1 UV–VIS experimental data and results

Types of LB films		X	Y	Z
$\beta' = 0°$	$A_{//}$	0.301	0.314	0.309
	$A_{\perp}$	0.308	0.336	0.315
	D_0	0.977	0.935	0.981
$\beta' = 30°$	$A_{//}$	0.349	0.353	0.359
	$A_{\perp}$	0.323	0.351	0.333
	D_{30}	1.081	1.006	1.078
$<\cos^2\theta>$		0.765	0.620	0.699
$<\cos^2\phi>$		0.457	0.428	0.473
$<\theta>$		29.0°	38.1°	33.2°
$<\phi>$		47.5°	49.1°	46.6°

plane area of the molecule. As surface pressure increases, the hydrophilic carboxy group stays in the water while the rest of the molecule becomes 'tilted'. Yet, if we compare experimental area of approximately 80 Å^2 on the water surface with the cross-sectional area of the 'tilted' molecule on the substrate, which is about 160 Å^2 × cos 38° ≈130 Å^2 according to Table 1, there is a difference in area of 130 Å^2 − 80 Å^2 = 50 Å^2. We conclude that the orientation in the film on water is not preserved in the deposited film on the substrate, owing to the interactions between the molecules and the substrate during the deposition process.

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